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LASER WINDOW SURFACE FINISHING AND
COATING TECHNOLOGY

Morris Braunstein

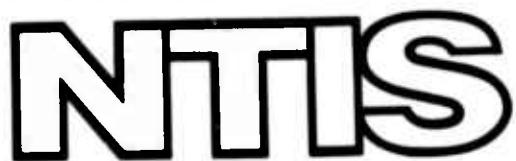
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) We report on the objectives and the progress achieved in a program to study the surface finishing and coating of laser windows. The program covers six technology areas: surface finishing, surface characterization, coating techniques, optical evaluation, chemical analysis, and laser window damage studies. Mechanical-chemical surface finishing results for KCl and ZnSe are discussed. Potassium chloride surfaces have been produced which result in KCl windows having improved		

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damage resistance of $>130 \text{ J/cm}^2$. Laser damage to antireflection coated ZnSe windows, at $10.6 \mu\text{m}$, appears to be limited to the bulk properties of ZnSe rather than to the surface or coatings. Germanium films produced by ion beam sputtering and by evaporation in ultrahigh vacuum onto KCl substrates have been evaluated and compared. The $10.6 \mu\text{m}$ calorimetric data and the chemical analysis of the Ge films obtained using Rutherford backscattering and Auger analysis are reported. The analysis results show evidence for the presence of K and Cl incorporation in the Ge films prepared.

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PREFACE

The author wishes to acknowledge the assistance of S. D. Allen and R.R. Turk for surface finishing studies, A.I. Braunstein and J.E. Rudisill for film deposition studies and evaluation of optical absorption of films, and R.R. Hart for surface analyses of coatings.

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I. INTRODUCTION

Hughes Research Laboratories (HRL) is engaged in a broad program to develop laser window surface finishing and coating technology. Extensive investigations are underway in many laboratories throughout the country, as well as at HRL to develop window materials that have both the low-optical absorption and the high tensile yield stress necessary to satisfy system applications. Two classes of materials — the wide bandgap semiconductors and the alkali halides — have received major emphasis in these investigations. The goal of our program at HRL is to investigate the surface characteristics and the optical coatings applied to laser windows in order to develop optimized finishing and coating procedures so that the laser damage thresholds of the coatings and surfaces approximate as closely as possible the damage thresholds of the bulk window materials. At present, serious limitation to window performance characteristics can exist because as the laser pulse duration is shortened and the peak power densities rise, the low damage threshold of some of the presently available coatings and surfaces can cause damage to occur below the bulk material damage threshold. This lowered damage threshold caused by the presence of pores and microcracks which can be present in window surfaces and coatings was the subject of a report by Bloembergen and Stickley,¹ which focused early attention on the importance of launching a research effort on surfaces and coatings to provide improvements in the state of the art.

This report presents preliminary results we have achieved to date in our program with emphasis on initial results for surface finishing of KCl and ZnSe, coating results for Ge films produced by evaporation in ultrahigh vacuum and by ion beam sputtering. The 10.6 μm

¹ N. Bloembergen and C.M. Stickley, Report of the ARPA 1972 Materials Research Council, E.E. Hucke, Editor, University of Michigan (1972).

calorimetric data and the chemical analysis of the Ge films obtained using Rutherford backscattering and Auger analysis will be reported and some preliminary data for laser damage to KCl and ZnSe.

II. TECHNICAL DISCUSSION

A. Surface Finishing

Conventional optical surface finishing techniques used in the optical industry use mechanical grinding, lapping, and polishing procedures which make it very difficult to attain surfaces of high grade optical finish on materials that are as soft as those under investigation for use as IR windows. In our work, we are studying ion beam polishing procedures and mechanical-chemical, etch-polish techniques for obtaining optical surfaces that are free of surface scratches and digs and that have surface work damage minimized. The mechanical-chemical polishing for KCl and ZnSe have given us early results which are promising in that they produce lower 10.6 μm absorption in the finished optical blanks and the surfaces have much improved laser damage resistance.

1. KCl Finishing

The mechanical-chemical polishing techniques for KCl we are using are an extension of the KCl finishing procedures reported by Braunstein, et al.² The technique reported in that work has been complemented with a final chemical etching procedure using concentrated HCl based on the work reported by Davisson³ of the U.S. Naval Research Laboratory.

In our experiments, 25 mm by 9 mm thick blanks of HRL reactive atmosphere process (RAP) grown KCl were sliced from a crystal boule with a wire saw and mechanically polished to a "window" finish and potted in Carbolene plastic film. The samples were subjected to a series of three-minute etches in reagent grade concentrated HCl after removal of the Carbolene layer then followed by a rinsing with 100%

²M. Braunstein, A.I. Braunstein, and J.E. Rudisill, Proceedings, Conference on High Power Infrared Laser Window Materials, Carl A. Pitha, Editor (1972).

³J. W. Davisson, Proceedings, Conference on High Power Infrared Laser Window Materials, Carl A. Pitha, Editor (1972).

ethanol (glass wash bottle) and drying in a dry nitrogen stream. The initial samples were not agitated during the three-minute etch and after the third etch (total nine minutes). Most of the initial polishing scratches as observed under 500x optical magnification (Bausch and Lomb Research Metallograph) were removed. The surface was generally smooth between the remaining scratches and grain boundaries, although some small roughly circular marks were observable which looked like rinsing marks. After a fourth three-minute etch definite etch pits were evident on the surface under the same magnification. Surfaces etched in HCl even for a short period of time do not show evidence of the surface fogging that occurs on polished surfaces produced using only mechanical finishing.

An optically polished window blank of the size referred to above, flat to approximately two fringes at 6328 Å was characterized immediately after polishing by absorption calorimetry, dark, bright, and oblique field optical microscopy and phase contrast microscopy. The latter technique tends to show subsurface damage that normally cannot be seen with the other optical microscope techniques. The same tests were repeated after two thirty-second etches in concentrated HCl with agitation followed by ethanol rinsing and drying as discussed above. The results are shown in Figs. 1 through 4(a), (b), and (c), respectively. Figure 5 shows a scanning electron microscope photograph (SEM) taken at ~15,000x. In Fig. 6(a), (b), and (c) are shown additional SEM photographs of a typical etched sample KCl surface at 9,000x, 18,000x, and 18,000x, respectively, at a beam voltage of 20 kV and $\approx 70^\circ$ tilt to the sample surface. Views a and b are of a surface region near grain boundaries and c is of a more typical surface region. The photograph in Fig. 1(c) shows no scratches or blemishes observable at 500x magnification other than grain boundaries. Twyman-Green interferometer photographs indicate that the flatness deteriorated by about a factor of two as a result of the total one-minute etch. The 10.6 μm absorption was reduced for KCl surfaces etched in HCl using the above procedures. Hughes Research Laboratories RAP grown KCl crystals after mechanical polishing have absorptions in the range of 0.0003 cm^{-1} to 0.0005 cm^{-1} , after chemical etching absorptions are in the 0.00015 cm^{-1} to 0.00020 cm^{-1} range.

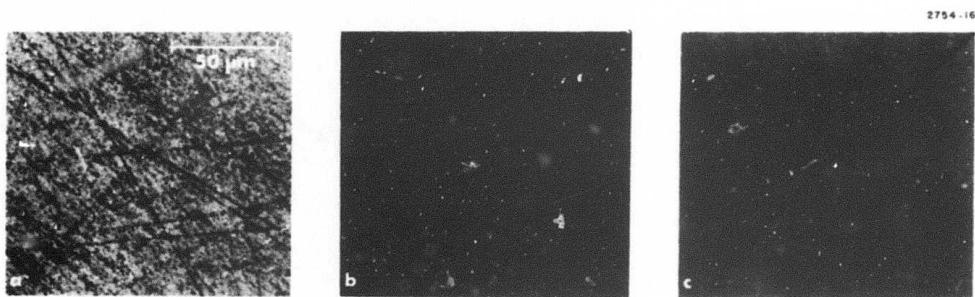


Fig. 1. Optical micrographs of KCl under bright field illumination, magnified 500 times.

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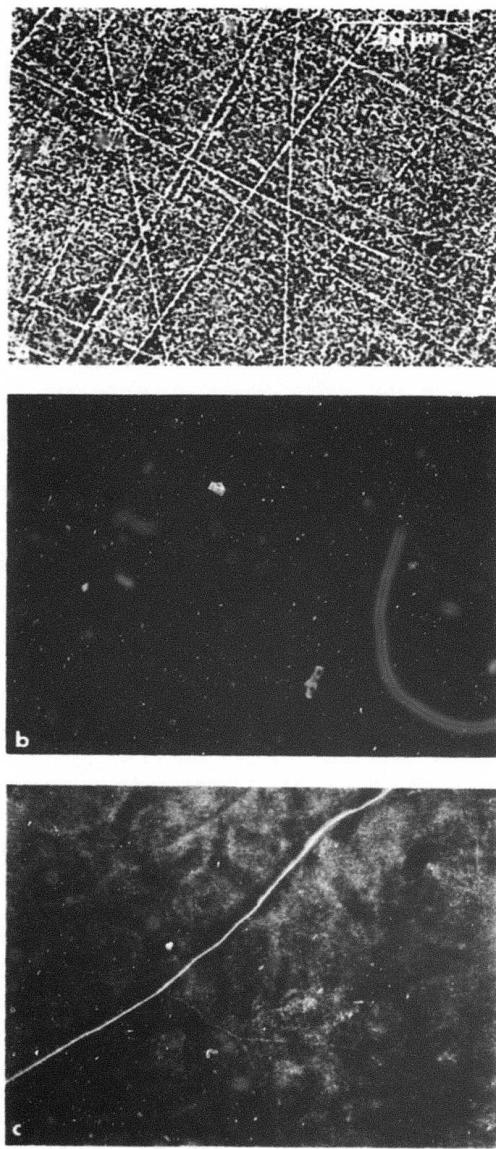


Fig. 2. Optical micrographs of KCl under oblique lighting conditions, magnified 500 times.

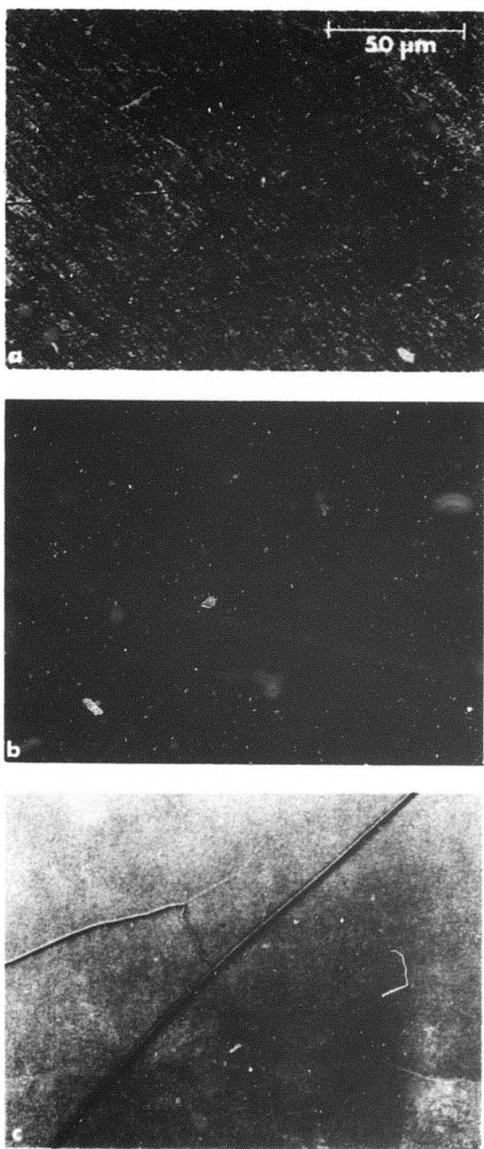


Fig. 3. Optical micrographs of KCl under dark field illumination, magnified 325 times.

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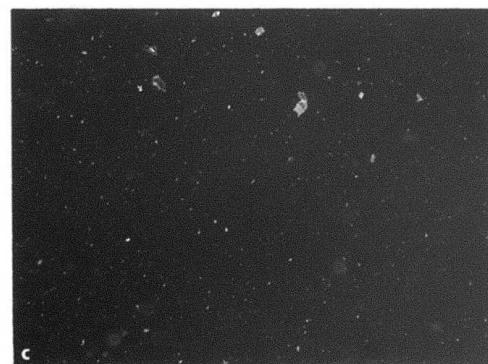
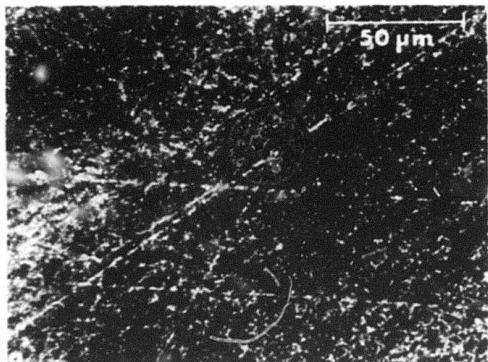


Fig. 4. Optical micrographs of KCl under phase contrast illumination, magnified 325 times.

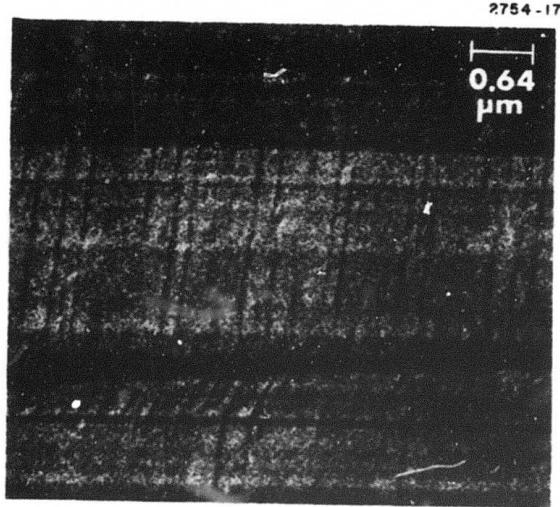
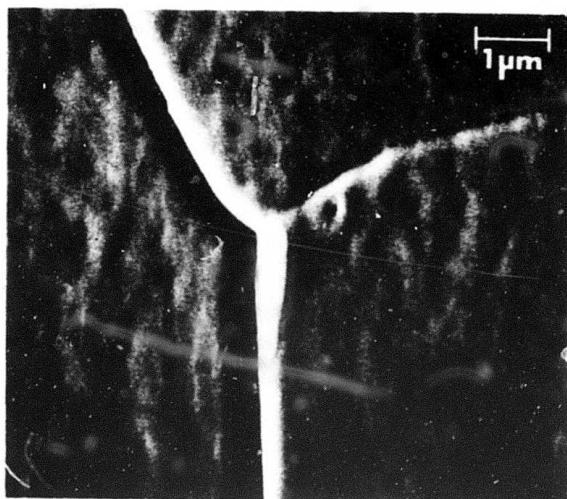


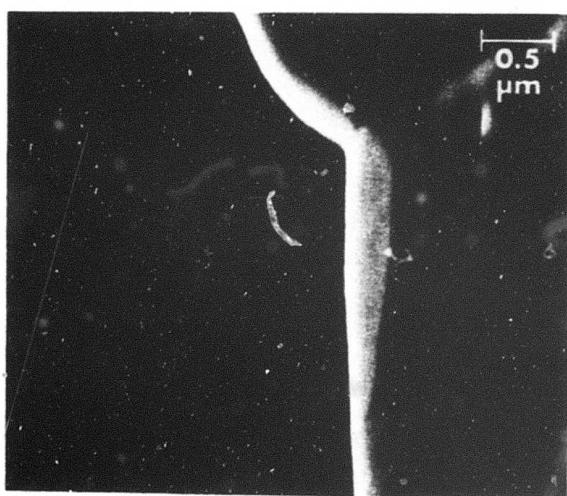
Fig. 5.
SEM surface topography of KCl sur-
face mechanically polished and
etched in HCl at a magnification
of 15,000 times.

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(a)

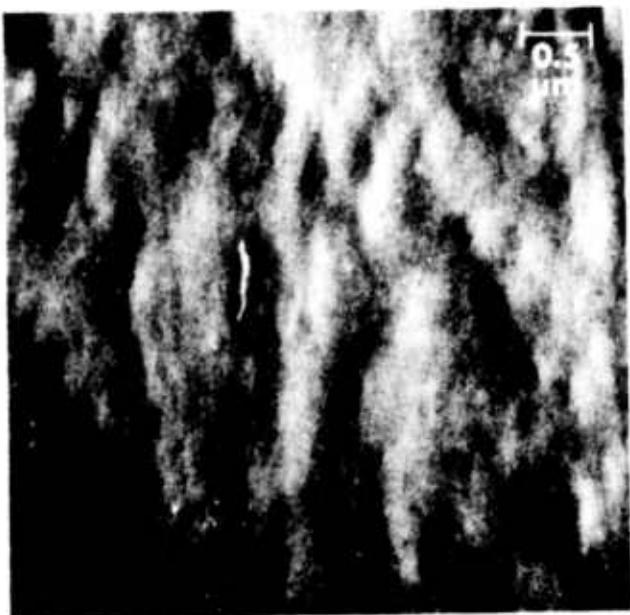
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(b)

Fig. 6. SEM photographs of KCl surface
at a beam voltage of 20 kV.

2754-18



(c)

BEAM $\approx 70^\circ$ TO SURFACE

Fig. 6(c). Continued.

An attenuated total internal reflection plate (ATR) 5 cm x 2 cm x 2 cm with 45° angles at entrance faces was fabricated from RAP KCl using mechanical surface polishing procedures. Initial scans on a Beckman IR 12 spectrophotometer showed several absorption bands, some of which could be attributed to hydrocarbon C-H stretch absorptions. Hydrogen chloride etching for 50 sec removed all but one of the absorption bands and a remaining absorption seen at 8.2 μm is believed to be characteristic of the ATR attachment to the Beckman.

Further work is in progress to determine the etch rate under standardized conditions and to improve rinsing and drying conditions. Improved rinsing and drying are being attempted using Freon TF vapor degreasing as a last step in the etching procedures after the ethanol rinse. This last cleaning and drying step to date has resulted in a more reproducible and cleaner finished surface.

Figure 7(a) and 7(b) show some recent results we have obtained for HCl etching of two press-forged KCl samples. One had been forged some time ago (2-20-73) and the second shown in view (b) was forged recently (10-31-73). These results indicate that the recrystallization induced by forging of undoped halides (to provide increased strength to the material) under the circumstances of the forging conditions used here did not result in a stable crystal structure. Upon aging, the sample produced earlier has reverted back to a predominately larger grained single crystal structure. The forging conditions used for the two samples which were pressed from starting blanks 1 in. thick are:

2-20-73 was deformed in two steps, 60% at 200°C and 15% further at 150°C at a strain rate of 0.050 in. min⁻¹/in. of remaining length.

10-31-73 was deformed 72% at 150°C at a strain rate of 0.050 in. min⁻¹/in. of remaining length.

The final pressure for the above two samples was 4000 psi; sample 2-20-73 when first forged evidenced a grain size of 1 μm to 10 μm after forging. Measurements made on the same piece 10-19-73 showed very large grains (several mm) with some small areas of 1 to 10 μm crystallites. Sample 10-31-73, when measured after HCl surface

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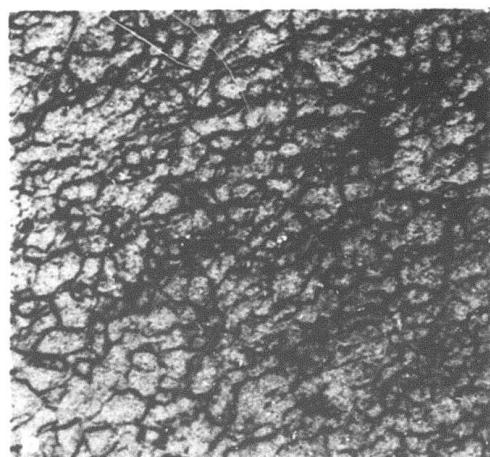
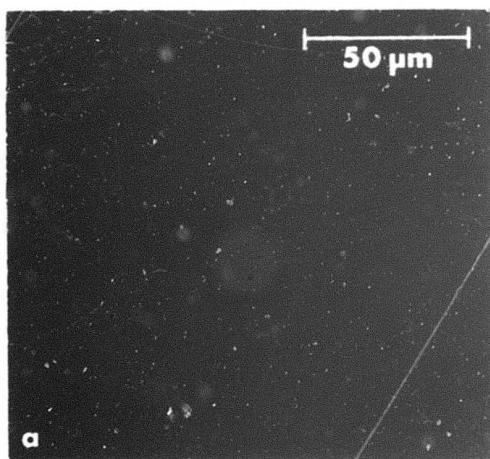


Fig. 7.
Optical micrographs of press-
forged KCl after 1 min HCl etch.

etching of the forging, indicated material with 1 to 10 μm grain size over the entire surface as shown in Fig. 7(b). Both samples were HCl etched for 1 min.

2. ZnSe Finishing

Surface finishing of zinc selenide for use as an infrared window for some laser system applications requires flatness to within $\lambda/20$ at 10.6 μm and parallelism to 20 sec of arc. In our work we have been able to meet these requirements using mechanical optical grinding and polishing techniques. These involve grinding the window blanks flat on cast iron laps using Al_2O_3 abrasives, followed by final polishing on pitch laps with fine alumina, still retaining flatness and parallelism.

Optical examination of surfaces of ZnSe finished in the above manner when examined under bright-field illumination reveal some scratches plus surface digs, resulting from surface pullout caused by the mechanical finishing operations. Further examination of the surface using transmitted light with phase contrast optical equipment reveals a multitude of scratches. We interpret these to be subsurface scratches, since they are not visible using brightfield or darkfield illumination. In addition to these subsurface scratches, one can see a faintly-revealed twinned-grain structure. Phase contrast examination reveals differences in refractive index, so scratches and twinned structure are visible as a result of index changes caused by strain or rearrangement of crystalline structure.

Mechanical removal of surface material by scraping with a metal blade revealed the well-defined twinned structure as seen in the photograph, Fig. 8(a), at 325x magnification. This has led us to deduce the following:

- a. The mechanically polished ZnSe surface layer is softer than the underlying crystalline substrate.
- b. The surface layer is caused by smearing of the surface during lapping in the near-final polishing stages, since scratches are positioned within the layer and result from finer abrasives.

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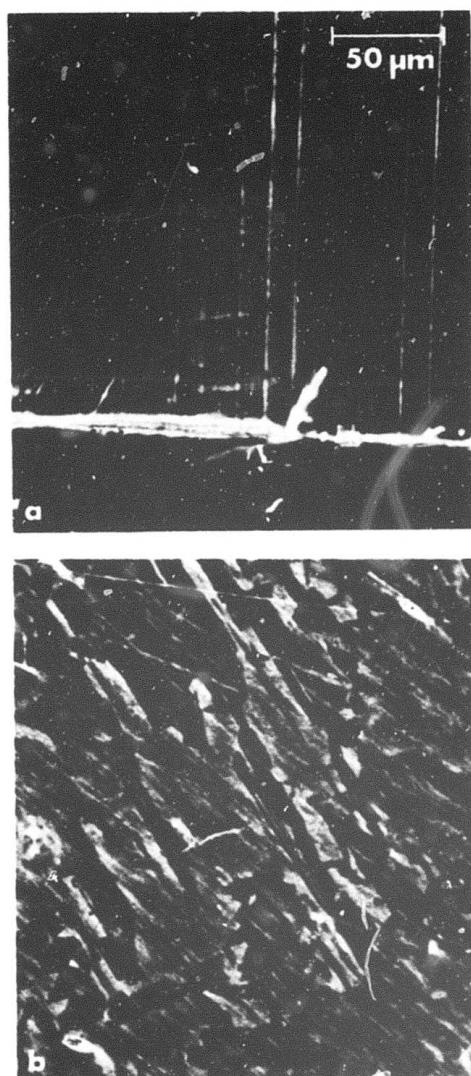


Fig. 8. Photomicrographs of zinc selenide surfaces at 325 times magnification after removal of polished surface layer.

- c. We have estimated that the surface layer is thin, about 5000 Å, and amorphous, since no structure is seen in the layer itself.

Removal of most of the surface layer of the ZnSe has been done in our preliminary work by metallographic polishing (fine alumina on a slow fine-cotton lap) as shown in Fig. 8(b). Our efforts to remove this smeared layer were based on our belief that removal of this layer would reduce surface optical absorption at 10.6 µm and contribute to the application of better adhering optical coatings to the ZnSe surfaces.

In view of the high free-energy of the smeared polished layer, we have assumed that rate of attack by a chemical etchant should be sufficiently greater than that of the crystalline subsurface, so that a combination etch-polish technique should give a crystalline surface free of distortion and representative of the bulk material, thus leading to reduced 10.6 µm absorption at the surface.

Our efforts to date along the lines of developing a mechanical-chemical etch-polish finishing procedure for ZnSe have led to a procedure outlined below.

ZnSe Etch Polish Procedure

1. Grind: Flat and parallel using Al_2O_3 microgrit (5 to 9 µm particle size) on a cast iron lap. Starting with 9 µm and ending with 5 µm grit.
2. Polish: Pitch lap using Linde A abrasive, 3 to 4 h polishing time to remove surface digs and pits.
3. Wash: Clean polished surface in warm H_2O to remove all traces of abrasives.
4. Etch: Immediately, 2 min etch polish after step (3) using alkaline $\text{K}_3\text{Fe}(\text{CN})_6$.*
5. Clean: Use soap solution (ORVUS), rinse in warm H_2O .
6. Rinse: Rinse and dry using pure ethanol.

* $\text{K}_3\text{Fe}(\text{CN})_6$, 90 grams; KOH, 1.7 grams; H_2O , 300 grams.

Figure 9(a) shows a 325x photograph of a mechanically polished ZnSe surface using steps (1) and (2) outlined above. Figure 9(b) shows a 325x photograph of the same ZnSe surface after final etch polishing. The crystalline grain structure of the ZnSe can be clearly observed. (The ZnSe we are using in our work is CVD material produced by Raytheon Corporation.) Using the complete step wise procedure outlined above we have been able to reproducibly produce polished ZnSe windows that have less than 0.005 cm^{-1} optical absorption at $10.6 \mu\text{m}$. Using windows polished this way, antireflection coatings can be applied to the window surfaces that meet program goals for an AFML sponsored program reported by M. Braunstein, et al., in the Proceedings, Conference on High Power Infrared Laser Window Materials. (Program goal is to produce coated windows that have 0.1% reflectance and absorptance at $10.6 \mu\text{m}$.)

3. Ion Polishing of ZnSe

It is well known that mechanical polishing can induce damage in the surfaces of semiconductor materials. Acceptable surfaces should only contain crystal flaws such as dislocations and inclusions that are characteristic of the bulk material and are not artifacts of the processing steps themselves. Sawing, abrasive lapping, polishing and mere handling can induce damage in materials. The degree to which mechanical polishing can damage laser materials in general is not completely known or understood, but some of our preliminary results on the effects of ion beam polishing of ZnSe show that under a restricted range of conditions surface optical absorption and surface optical scattering at $10.6 \mu\text{m}$ can be reduced below the level that exists right after the ZnSe surface has received its final mechanical polish.

In a recent ion polishing experiment, for example, a ZnSe window blank that had its surface mechanically polished had an α at $10.6 \mu\text{m}$ of 0.0069 cm^{-1} ; the same blank after having its surface ion polished

⁴M. Braunstein, J.E. Rudisill, and A.I. Braunstein, "Optical Coatings for High Energy ZnSe Laser Windows," Proceedings 3rd Conference on High Power Infrared Laser Window Materials, Carl A. Pitha, Editor, to be published (November 1973).

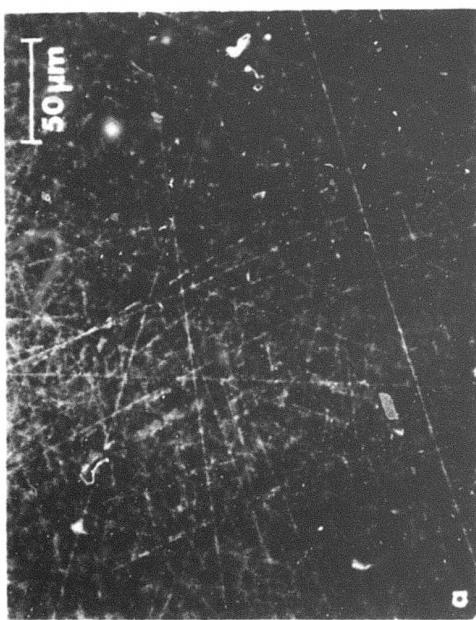
MECHANICAL/CHEMICAL POLISH

Fig. 9. Photomicrographs of zinc selenide surfaces at 325 times magnification, after mechanical polishing and after final etch polishing.

MECHANICAL POLISH



b



a

2754-2

with argon for a short time period had an α reduced to 0.0044 cm^{-1} . After continuing the ion polishing for a longer time period the α of the blank increased to 0.0110 cm^{-1} . During this same ion polishing sequence the optical scattering at $10.6 \mu\text{m}$ increased tenfold over the value that existed right after mechanical polishing.

We have not yet established the optimum conditions for receiving any benefits from ion beam surface treatment for ZnSe. The parameters that have to be varied and controlled to standardize the process for optimization of the technique are: sample rotation, angle of argon ion sputtering beam to the blank surface, ion beam energy, ion current density, and time of ion etching. It is clear, however, from the reduction in the surface optical absorption achieved in the results referenced above for the initial stages of ion surface bombardment that some benefits are to be had from a continued investigation of ion polishing techniques.

B. Surface Characterization

1. Rutherford Backscattering and Ion Channeling Analyses

a. Polishing Damage in KCl

The energy spectra of Rutherford backscattered light ions (H^+ and He^{++}), which are incident in a random direction and along a major channeling axis of a target crystal, provide quantitative information of both the amount and depth distribution of lattice disorder. Such measurements have been especially useful for the study of ion-implantation-produced disorder in Si, Hart and Davies.⁵ We have extended this technique to the study of polishing damage in KCl single crystals.

The experimental arrangement is illustrated in Fig. 10. Back-scattered particles are detected at an angle of 160° with respect to the incident beam using a cooled Si detector (full width at half maximum

⁵ R.R. Hart Radiation Effects **6**, 51 (1970), J.A. Davies, J. Denhartog, L. Eriksson, and J.W. Mayer, Can. J. Phys. **45**, 4053 (1967).

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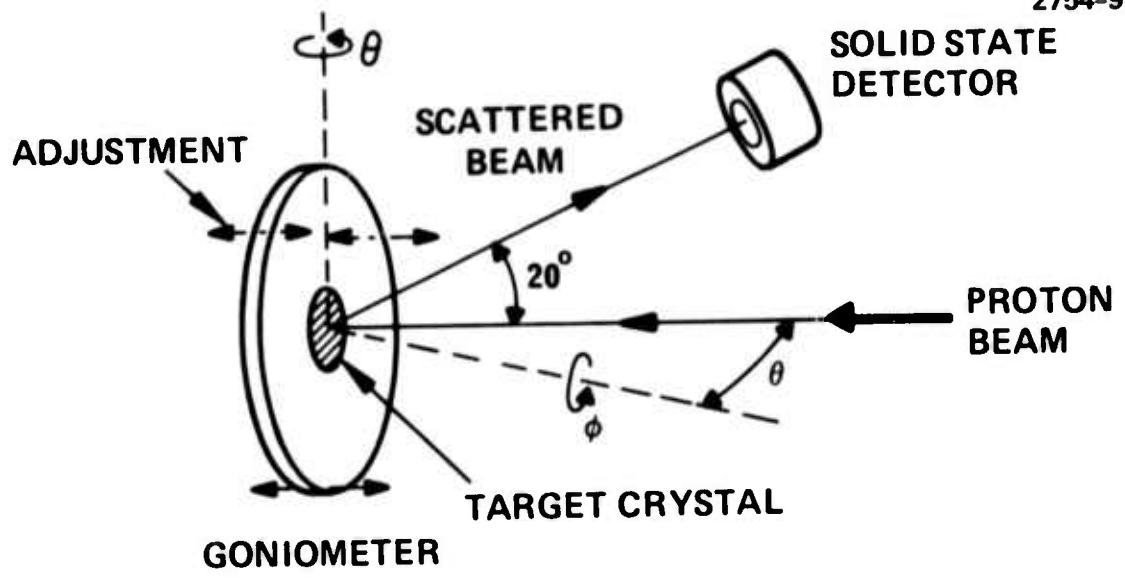
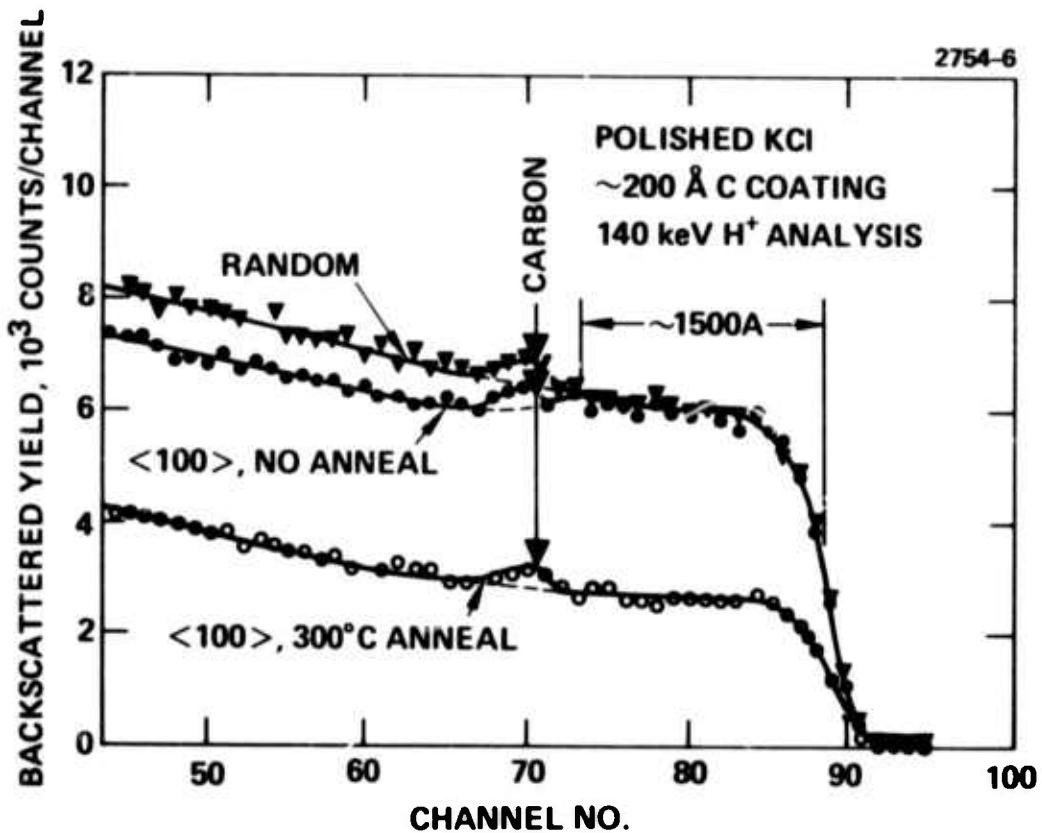


Fig. 10. Schematic of ion backscattering target chamber.

~ 5 keV for H^+). The sample is mounted on a goniometer to permit either $<100>$ or random alignment of the crystal with respect to the incident beam. An oven assembly which encloses the sample holder permits *in situ* anneals. A biased W filament may be used to provide electron flooding of the target when necessary to prevent beam charging effects.

The samples used for this work were single crystal platelets of KCl (Optovac) which were cleaved along $\{100\}$ planes and then polished with either Linde A or Linde B abrasive on flannel using methanol. Backscattered energy spectra of 140 keV H^+ incident in random and $<100>$ directions before and after 30 min anneal at $300^\circ C$ on a Linde B polished sample are shown in Fig. 11. In this case, a 200 Å carbon layer was deposited on the specimen to prevent beam charging. Before anneal the coincidence of the $<100>$ and random yields from the surface to a depth of about 1500 Å indicates that an amorphous layer was formed to this depth by the mechanical polishing. At deeper depths (smaller channel numbers), the $<100>$ yield is less than the random yield as a result of ion channeling in at least partially crystalline material. However, long range disorder or strain is suggested since, even though the beam is significantly dechanneled in traversing the amorphous layer, the $<100>$ yield does not decrease as much as expected if the substrata were perfectly crystalline below the amorphous layer. The small peaks near channel 70 are caused by the carbon coating. A $<100>$ backscattered energy spectrum taken after the anneal sequence is also shown in Fig. 11. As can be seen, the $<100>$ yield is about one-half of the random yield, indicating about 50% recrystallization of the amorphous layer and thus comparable ion channeling. Clearly, either longer times or higher anneal temperatures are required to effect complete recrystallization. Nevertheless, the data of Fig. 11 indicate that significant reduction in polishing damage occurs after relatively mild thermal treatment.



ANALYSIS ION: H^+ AT 140 keV
 POLISH: LINDE B - METHANOL ON FLANNEL
 ANNEAL: 30 min AT 10^{-6} Torr

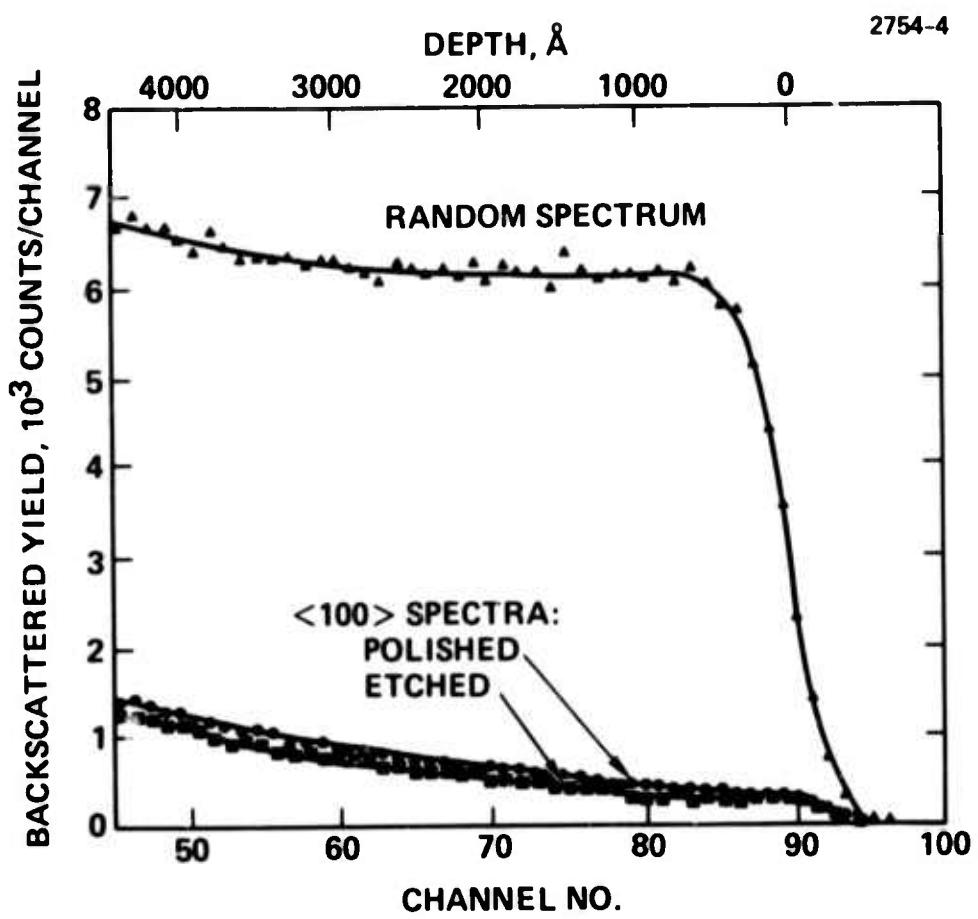
Fig. 11. 140 keV H^+ channeling analysis of polished KCl before and after 300°C anneal.

Backscattered energy spectra of 140 keV H^+ from both a Linde A polished sample and a sample etched for 30 sec in HCl are shown in Fig. 12. In these cases electron flooding prevented beam charging. As can be seen in Fig. 12, the $\langle 100 \rangle$ backscattered yield of the etched sample near its surface is about 1/20 of the random yield. Such a ratio is consistent with good crystalline qualities. The small peak at the surface (channel 90) is probably caused by a thin surface oxide. Although the $\langle 100 \rangle$ yield of the polished sample is somewhat greater than that of the etched sample, indicating some lattice disorder or strain, it is remarkable that no amorphous layer is observed as was seen on the Linde B polished sample of Fig. 11. In fact, greater than 90% of the beam remains channeled in the surface region.

Subsequent attempts to reproduce the 1500 Å amorphous layer by polishing with Linde B abrasive also led to little damage. Furthermore, the presence of a 200 Å carbon coating was found to have negligible effect on lattice disorder. Thus, at this time, we can only conclude that the amount of polishing damage is affected by an unknown variable and may be either very little or completely amorphous. However, the fact that very little polishing damage may be produced suggests that polishing may not always strongly affect the surface perfection of KCl.

b. Backscattering Analysis of Germanium Films

Rutherford backscattering analysis has been used in some preliminary experiments to compare the properties of Ge films on KCl produced in ultrahigh vacuum (UHV) and by ion beam sputtering. Figures 13 and 14 show the results of a comparison of UHV-prepared thin Ge films deposited on KCl at a low rate and a somewhat higher rate, 0.6 Å/sec and 27 Å/sec, respectively. A 2700 Å film deposited at the low rate has a $10.6 \mu m$ absorption coefficient of 94 cm^{-1} and the more rapidly deposited film with a thickness of 8800 Å has a lower absorption of 24 cm^{-1} . The backscattered energy spectra also reveal, when compared, that there is some evidence for presence of heavy metal impurity (possibly tungsten), oxygen, and potassium. The concentration of these impurities is somewhat lower

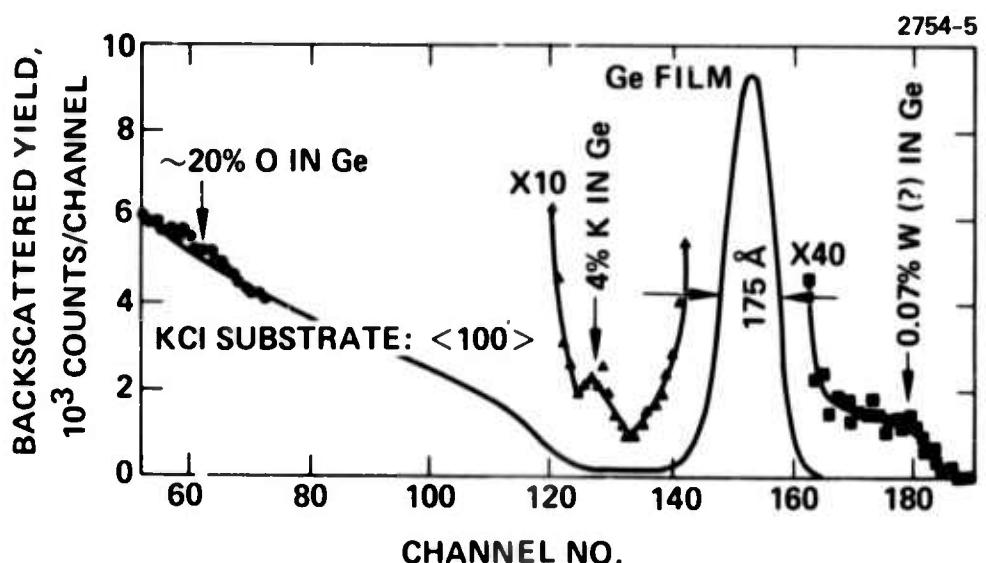


ANALYSIS ION: H^+ AT 140 keV

POLISH:
LINDE A - METHANOL ON FLANNEL

ETCH:
30 sec IN HCl

Fig. 12. 140 keV H^+ channeling analysis of polished and etched KCl.



ANALYSIS ION: He^{++} AT 280 keV

SAMPLE 8-21-73 U

DEPOSITION CONDITIONS:

RATE: 0.6 \AA/sec

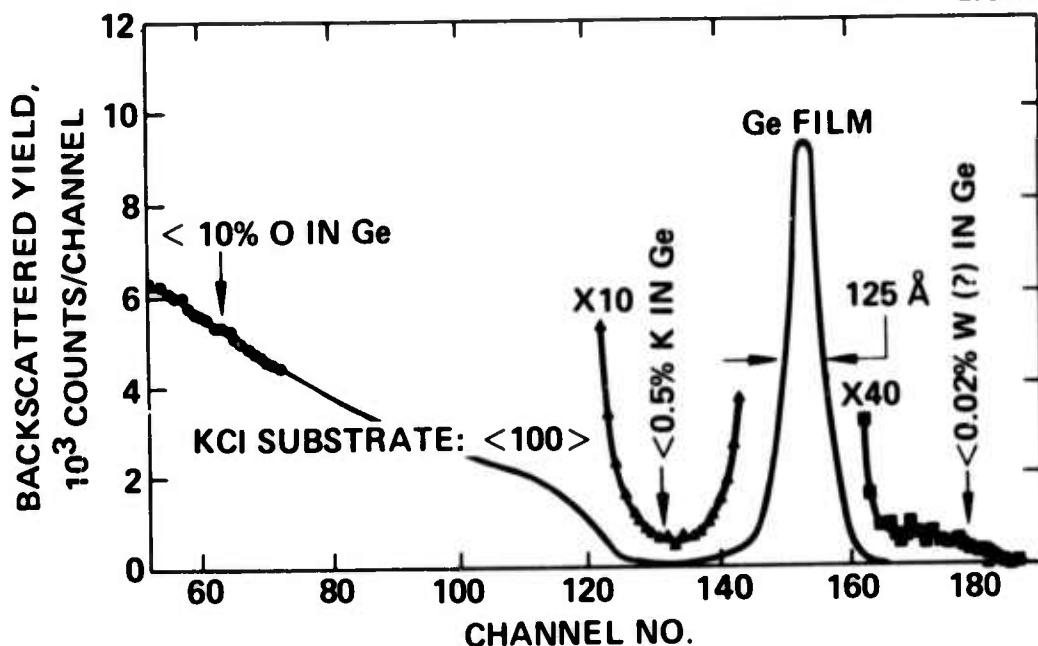
PRESSURE: $8 \times 10^{-10}\text{ Torr}$

SUBSTRATE TEMP.: 150°C

2700 \AA Ge ON KCl, $\alpha = 94\text{ cm}^{-1}$

Fig. 13. Backscattered energy spectrum of 280 keV He^{++} incident on a 175 \AA UHV deposited Ge film on KCl.

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ANALYSIS ION: He^{++} AT 280 keV

SAMPLE 9-25-73 U

DEPOSITION CONDITIONS:

RATE: 27 \AA/sec PRESSURE: $2 \times 10^{-8} \text{ Torr}$ SUBSTRATE TEMP.: 150°C $8800 \text{ \AA Ge ON KCl}, \alpha = 24 \text{ cm}^{-1}$

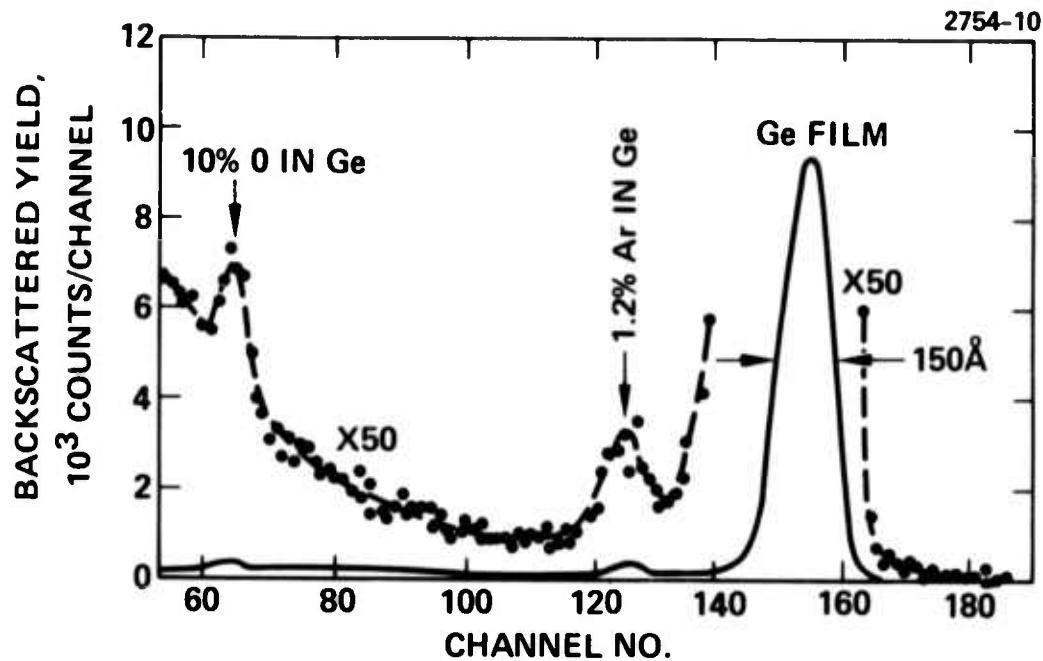
Fig. 14. Backscattered energy spectrum of 280 keV He^{++} incident on a 125 \AA UHV deposited Ge film on KCl.

in the data shown in Fig. 14 for the more rapidly deposited Ge film. The most surprising result of the analysis of these films has been the presence of the potassium which we believe diffuses into the Ge film from the substrate. We do not know at the present time the influence the potassium content has on the optical absorption properties of the Ge films.

Figure 15 shows the backscattering energy spectrum for a Ge film produced by ion beam sputtering onto a carbon substrate. The carbon substrate was used to enable our achieving increased sensitivity for the analysis of oxygen content in the film. In previous experiments we have determined that the carbon support structure had an oxygen level very much reduced below that shown in the data of Fig. 15. The spectrum shown indicates the presence of 1.2% argon and 10% oxygen in the Ge film. A 6000 Å Ge film produced on KCl during the same ion sputtering deposition had an optical absorption coefficient at $10.6 \mu\text{m}$ of $36 \pm 12 \text{ cm}^{-1}$.

Auger electron analysis of the Ge film produced in UHV at the low rate of 0.6 \AA/sec was performed to determine if the potassium found in the film using ion backscattering analysis would be confirmed by Auger analysis. As can be seen in Fig. 16, the Auger spectra produced by ion beam sputter profile analysis do indeed provide further evidence that the Ge film deposited on KCl does indicate possible diffusion of the substrate material into the film, as evidenced by the Cl and K peaks.

In Fig. 17 electron microprobe analysis of UHV deposited Ge on KCl is shown for a Ge film produced by T. Donovan of the Naval Weapons Center, China Lake. The $10.6 \mu\text{m}$ absorption coefficient for this film was measured at HRL to be 77 cm^{-1} . The probe analysis showed the presence of K, Cl, and Cu impurities in the film at 0.8%, 0.9%, and 0.4% levels, respectively. It should be noted that the relatively high, 77 cm^{-1} value, for the Ge film absorption occurs for a rate of deposition which is low compared with the data for our film shown in Fig. 14, which was 27 \AA/sec . This trend for Ge films showing high absorption when produced at low rates is consistent for films



ANALYSIS ION: He^{++} AT 280 keV

DEPOSITION CONDITIONS:

RATE: 0.5 Å/sec

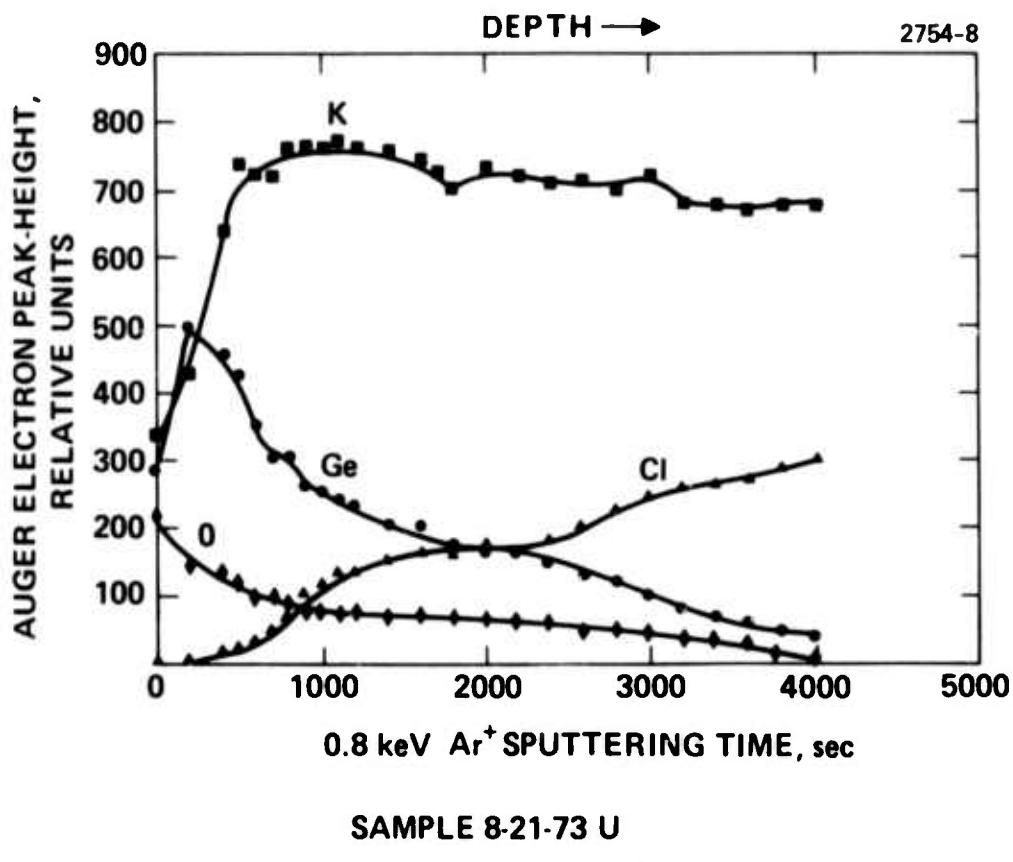
ION: Ar^+ AT 7.5 keV

PRESSURE: 2×10^{-5} Torr (Ar), 5×10^{-7} Torr (BASE)

SUBSTRATE TEMP.: 80°C

6000 Å Ge ON KCl, $a = 36 \pm 12 \text{ cm}^{-1}$

Fig. 15. Backscattered energy spectrum of 280 keV H^{++} incident on a 150 Å Ge film sputter-deposited onto a carbon substrate.



SAMPLE 8-21-73 U

DEPOSITION CONDITIONS:

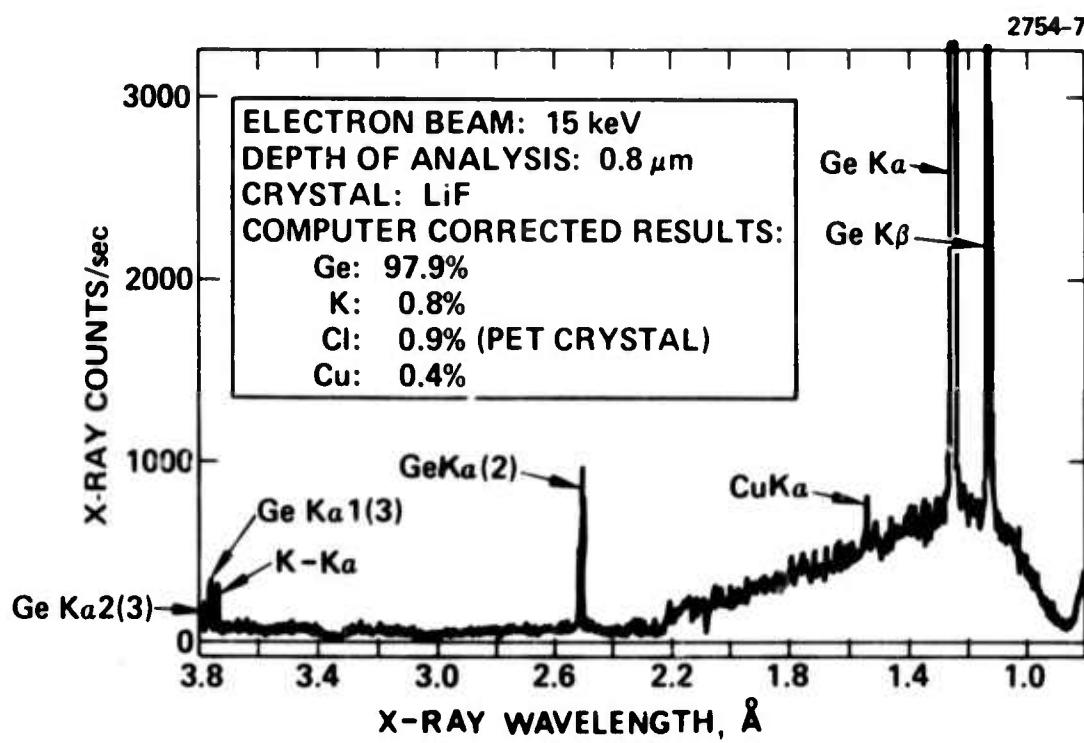
RATE: 0.6 Å/sec

PRESSURE: 8X10⁻¹⁰ Torr

SUBSTRATE TEMP.: 150°C

2700 Å Ge On KCl, $\alpha = 94 \text{ cm}^{-1}$

Fig. 16. Auger electron analysis of a 175 Å UHV deposited Ge film on KCl.



SAMPLE: DONOVAN #1
DEPOSITION CONDITIONS:
RATE: 1-3 $\text{\AA}/\text{sec}$.
PRESSURE: 1×10^{-9} Torr
SUBSTRATE TEMP.: AMBIENT
ANNEAL: 100°C FOR 2 hr
THICKNESS: 1.24 μm
 $a = 77 \text{ cm}^{-1}$

Fig. 17. Electron microprobe analysis of a 1.24 μm UHV deposited Ge film on KCl. Film produced at Naval Weapons Center, China Lake.

produced in oil-pumped vacuum systems too, as will be shown in the table for Ge film data presented later in this report.

C. Coating Techniques

During the course of our program, it is our objective to prepare film coatings for candidate IR laser window materials by three film preparation techniques: ultrahigh vacuum deposition, ion beam sputtering, and chemical vapor deposition. Because our program was recently started, May 1973, all three film preparation technology areas are not completely implemented to produce films which can be compared one with another. We will present here some of the preliminary results we have achieved and the status to date, mainly for UHV preparation.

1. Ultrahigh Vacuum Film Deposition

The first film material under evaluation is germanium. The results for germanium films prepared in UHV have been compared with results for ion sputtered germanium, to prior results for germanium evaporated in conventional vacuum, and to UHV results obtained by T. Donovan at NWC, China Lake. The prior HRL results in conventional vacuum showed that e-gun evaporation at high rates was necessary to avoid high absorption at $10.6 \mu\text{m}$ which was caused by the tail of a $13 \mu\text{m}$ absorption band present in films prepared at low rates of deposition.

The data obtained to date are shown in Table I. The trend shown in the data reported in the table is that lower absorption Ge films are produced at the higher rates of deposition. The germanium film with the lowest absorption, 10 cm^{-1} , was produced on a ZnSe substrate using ion beam sputtering. A comparable absorption of 12 cm^{-1} for a film produced on KCl in UHV was obtained at the highest deposition rate of 70 \AA/sec as shown in the table for sample number 7-23-73U. The Ge film prepared by T. Donovan referenced in Fig. 17 had an absorption of 77 cm^{-1} for a 1 to 3 \AA/sec deposition rate under UHV conditions.

TABLE I
Germanium Film Data

Sample Number	Preparation Technique	Pressure During Deposition, Torr	Substrate	Substrate Temperature, °C	Deposition Rate, Å/sec	10.6 μm Absorption, cm⁻¹
B11-9	E-gun in conventional vacuum	2×10^{-6}	RAP KCl	100	33	12 to 24 (13 μm absorption)
B24-4	Resistance source in conventional vacuum	2×10^{-6}	RAP KCl	50	4 to 5	~10,000
B-23-13	Ion beam sputtered in conventional vacuum	2×10^{-5} , Ar	RAP KCl	125	2 to 3	24 to 48
R20	Ion beam sputtered in conventional vacuum	2×10^{-5} , Ar	Raytheon ZnSe	125	2 to 3	10
7-23-73U	E-gun in UHV	1.5×10^{-7}	RAP KCl	Ambient	70	12
9-25-73U	E-gun in UHV	2×10^{-8}	RAP KCl (etched)	150	42	24
8-21-73U	E-gun in UHV	2×10^{-9}	RAP KCl	150	0.8	94

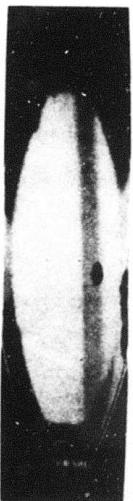
D. $10.6 \mu\text{m}$ Laser Damage

Our earlier work on laser damage to windows and window coatings at HRL supported by AFWL was reported by Braunstein et al.⁶ at the NBS Laser Damage Conference.

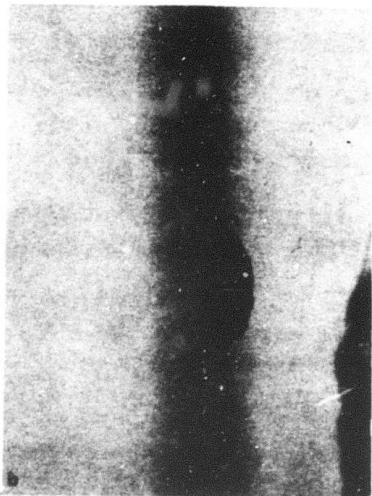
The laser damage effort under the present ARPA-supported program discussed in this report will not start according to plan until the latter part of November 1973. However, some preliminary data have been obtained for some of the KCl and ZnSe samples having surface finishes as described in the surface finishing section of this report. For HRL RAP-grown KCl single-crystal material having HCl chemical etched surfaces, damage thresholds achieved are $>140 \text{ J/cm}^2$ at power densities of $>230 \text{ MW/cm}^2$. Zinc selenide windows (Raytheon CVD material) polished at HRL and provided with antireflection coatings show no surface damage to the windows or coatings at the power levels we have available in our test laser ($\approx 230 \text{ MW/cm}^2$). However, damage does occur to the interior region of the bulk material at energy densities of 17 to 20 J/cm^2 and at power levels of 28 to 33 MW/cm^2 . Damage sites occur at regions in the window which show ZnSe material nonuniformity as evidenced by dark bands which show up in the window material when a window blank is viewed through the window edge using visible light. Figure 18(a) shows a photograph of such a damage site when viewed through the diameter of a window from a polished edge. Figure 18(b) is an enlarged view at $20\times$ magnification of the same test sample.

⁶A. I. Braunstein, V. Wang, M. Braunstein, J. E. Rudisill, and J. Wada, "Pulsed Laser Damage Studies of Windows and Window Coatings," NBS Spec. Publ., Laser Induced Damage in Optical Materials, A. J. Glass and A. H. Guenther, Editors (Government Printing Office, Washington, D.C., 1973).

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(ACTUAL SIZE) LASER BEAM ENTRY
FROM THE RIGHHAND SIDE OF
PHOTO



(20x MAGNIFICATION) LASER BEAM
ENTRY FROM THE RIGHHAND SIDE
OF PHOTO

Fig. 18. Photographs of zinc selenide window damaged by a
10.6 μm pulsed laser beam.

III. SUMMARY

The preliminary results we have achieved to date on our Laser Window Surface Finishing and Coating Technology Program have shown that consistently lowered $10.6 \mu\text{m}$ optical absorption can be obtained for single crystal KCl and CVD ZnSe windows using the mechanical-chemical etch procedures we have described in this paper. Improved laser damage resistance for KCl has been achieved and the damage to our present state-of-the-art antireflection coated ZnSe windows is bulk material limited and not limited by the window surface or coatings.

The results we have achieved for Ge film coatings indicate a pronounced dependence of the absorption coefficient on film deposition rate and Ge coatings on KCl show evidence for K and Cl impurity migration into the films from the window substrate. The best Ge films we have produced to date seem to be limited to an α of $\approx 10 \text{ cm}^{-1}$.

Rutherford backscattering analysis has been shown to be a useful tool for investigating surface damage in single crystal KCl caused by surface finishing operations and an equally useful tool for looking at impurity levels in Ge films. The unanticipated presence of the K and Cl in the Ge films produced on KCl focuses attention on the possibility that diffusion of species into film coatings from window surfaces and interpenetration of species in multilayer optical film coatings could have a pronounced effect on performance of coated IR windows.

IV. PLANS FOR NEXT PERIOD

We will continue our work covering the six program elements: surface finishing, surface characterization, coating techniques, optical evaluation, chemical analysis, and 10.6 μm laser damage studies. The work effort will still place emphasis on an integrated research program on the preparation of antireflective coatings for high power infrared laser window materials and the relationship of such preparative procedures to the transmissivity of the coated windows at infrared wavelengths and to the damage mechanisms of such optimally coated windows when subjected to high power infrared laser irradiations. The window materials which are to be investigated will include single and polycrystal KCl, CaF_2 , alloy alkali halides, and ZnSe. Selected chalcogenide and fluoride materials, either singly or in multilayer stacks, will be investigated for use as antireflectant coatings and the coatings will be evaluated for their infrared transmissivity, adhesion and optical performance under infrared laser irradiation.

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